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LOW TEMPERATURE ENERGY TRAPPING AND
EMISSION LINE PROFILE OF DISORDERED SOLIDS

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ABSTRACT

In a disordered solid, where random excitation energy and donor-acceptor separation is expected, low temperature energy transfer between a high energy excited molecule to a lower energy acceptor might not be complete. As a result, the emission profile of the solid at low temperature is determined by the energy distribution of the emission of the trapping sites. Predictions based on these ideas are used and a fit is made to the 4.2 °K observed phosphorescent profile of 1-bromo, 4-chloronaphthalene, an orientationally disordered molecular solid. The theoretical fit to the observed emission profile is discussed in terms of the possible energy transfer mechanism(s) in this solid.

Introduction

The characteristics of phonon assisted spectral diffusion in disordered materials have recently attracted considerable attention. Time resolved fluorescence line narrowing (TRFLN) studies of spectral diffusion within an inhomogeneously broadened impurity transition in host glasses^{1,2} and crystals³ at high temperatures (i.e. $kT > \Gamma$, the inhomogeneous width observed in absorption) have shown that the narrowed component typically decays preserving its width while the remainder of the inhomogeneous profile emerges uniformly and at long times resembles the absorption profile. Recent TRFLN studies of the $T_1 \rightarrow S_0$ transition of neat 1-bromo, 4-chloronaphthalene (BCN) have shown⁴ that only exothermic energy transfer from high to low energy sites is observed. The exothermic nature of the energy transfer in this system is manifested in the emission spectrum which is shifted to lower energy and is narrower than the corresponding absorption spectrum of the same transition⁵ suggesting only emission from the low energy sites.

In this letter we present the emission lineshape function for an inhomogeneously broadened absorption profile for $kT \ll \Gamma$, where only exothermic energy transfer occurs. An interaction radius is defined as the distance between donor and acceptor where the unimolecular radiative lifetime of the donor and the energy transfer time are equal.⁽⁶⁾ An energetically excited site with no lower energy sites within the interaction volume is considered trapped and will contribute to the emission profile. Those sites with lower energy sites within the interaction volume will transfer the excitation before radiating and will not be observed in emission. The emission profile in disordered solids at low temperatures will thus reflect the frequency distribution of the emission of the trapping sites. The results of this model show that as the number of sites contained in the interaction volume increases, the emission profile is shifted to lower energy and the emission width narrows.

We find that from the emission and absorption profiles, along with the radiative lifetime in the absence of energy transfer, one can determine the microscopic energy transfer parameters if the coupling mechanism and dimensionality of the energy transfer are known. The fit to the observed emission profile of the $T_1 \rightarrow S_0$ transition of BCN is found to be good with only one adjustable parameter, the number of sites within the interaction volume.

The emission lineshape function

In the model considered here, the inhomogeneously broadened absorption spectrum is assumed to be due to a random (uncorrelated) distribution of site energies. The effects of homogeneous broadening are taken to be much smaller than the absorption or emission linewidths and the oscillator strength is assumed constant across the band such that the distribution of site energies is represented by the absorption profile. The microscopic transfer rate between sites is taken to be independent of the energy of the sites between which energy transfer takes place, except that only exothermic energy transfer is allowed. For temperatures where $kT \ll \Gamma$, energy transfer is only possible from high to low energy sites since transfer from a low energy site to a high energy site requires the population of phonons which will be small at this temperature. For an excitation at energy ν_{exc} in a single component crystal one can describe the acceptor concentration as the mole fraction of sites having energy $\nu \leq \nu_{exc}$. Those sites with energy $\nu > \nu_{exc}$ will correspond to host sites since energy transfer from an excited site at energy ν_{exc} to higher energy sites will be negligible at low temperatures.

The decay of an energetically excited donor site in the presence of acceptors can occur by radiative and nonradiative unimolecular processes or by the donor transferring its excitation nonradiatively to an acceptor. The radiative and nonradiative

unimolecular processes are taken to be independent of the nature of the excited site and to occur with a rate of $1/\tau_0$, where τ_0 is the decay time of the excited state in the absence of acceptors. In the presence of acceptors the donor may transfer its energy nonradiatively through either multipolar or exchange interactions. The rate of energy transfer, $W(R)$, can be written as⁶

$$W(R) = 1/\tau(d/R)^s, \quad (1)$$

for multipolar interactions where τ is the nearest neighbor transfer time, d is the nearest neighbor distance, R is the donor-acceptor pair distance, and $s = 6, 8, 10$ for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively, and for exchange interactions

$$W(R) = 1/\tau_{\text{exp}}(\gamma(d-R)), \quad (2)$$

where γ is a measure of the dependence of the transfer rate on distance. For both types of interaction, the transfer rate is strongly dependent on the donor-acceptor distance. One can define an interaction radius,⁽⁶⁾ R' , as the donor-acceptor distance for which the energy transfer rate is equal to the unimolecular decay rate. From eqs. (1) and (2) one finds

$$R_0 = R'/d = (\tau_0/\tau)^{1/s} \quad (3a)$$

and

$$R_0 = 1 + 1/\gamma d \ln(\tau_0/\tau), \quad (3b)$$

for multipolar and exchange interactions, respectively, where R_0 is the interaction radius in units of the lattice spacing, d . The number of sites (excluding the one occupied by the donor) within the interaction volume, n , is given by

$$n = 4/3 \pi R_0^3 - 1 \quad (4a)$$

$$n = 2 \pi R_0^2 - 1 \quad (4b)$$

$$n = 2R_0 - 1 \quad (4c)$$

for 3-D, 2-D, and 1-D interactions respectively.

We now consider the steady state excitation of sites on the high energy side of the inhomogeneous profile where the probability of an acceptor site being in the interaction volume of the initially excited site is near unity. The initial excitation will thus transfer exothermally with unit probability. The exothermic energy transfer process continues until a site is reached for which no lower energy acceptors lie within the interaction volume. The excitation is thus trapped and will then radiate. Assuming that the initial excitation finds these trapped sites with equal probability, the emission profile will represent the energetic distribution of sites for which no lower energy acceptors lie within the interaction volume. The distribution of trapped sites can be obtained from calculating, as a function of ν , the product of the probability that a site at energy ν has no lower energy acceptors within the interaction volume and the relative number of sites at energy ν .

The probability that an energetically excited site has no lower energy acceptors within the interaction volume given by n is $(1 - \chi_\nu)^n$, where χ_ν is the mole fraction of acceptor sites and is dependent on the excitation energy, ν , of the site for the system considered here. For an inhomogeneously broadened single component crystal with a Gaussian absorption profile centered at ν_{\max} , the corresponding emission profile, $I(\nu)$, is given by

$$I(\nu) = \text{Const.} (1 - \chi_\nu)^n \exp(-\ln 2 ((\nu - \nu_{\max}) / \Gamma)^2), \quad (5)$$

where Γ is the Gaussian width (hwhm), and

$$\chi_\nu = \Gamma^{-1} (\ln 2 / \pi)^{1/2} \int_{\nu' \leq \nu} \exp(-\ln 2 ((\nu' - \nu_{\max}) / \Gamma)^2) d\nu' \quad (6)$$

For an optically active guest species in a spectrally inert host lattice where the guest species occupy the host lattice sites with probability p , (given by the overall mole fraction of the guest), equ. 5 holds with $\chi_\nu \rightarrow \chi'_\nu p$, where χ'_ν is

determined from the guest absorption profile using equation 6.

Results

In this section we present our results of the numerical evaluation of equation 5. The emission lineshapes for several values of n in the range of 10 - 10,000 sites for a single component disordered crystal are displayed in fig. 1, along with the Gaussian absorption profile. Fig. 1 illustrates that as the interaction volume gets larger, the emission profile is shifted further to lower energy and the emission linewidth narrows. These results can be understood with the physical model used here. For a particular energetically excited site, the probability of finding a lower energy acceptor site within the interaction volume grows with the interaction volume. The distribution of the emission frequency of the trapping sites is thus shifted to lower energy where the concentration of possible lower energy acceptors is smaller. The shift in the emission maximum from the absorption maximum and the emission linewidth vs. the interaction volume are plotted in figs. 2 and 3, respectively. From the absorption and emission spectra of a system, one can find n , the number of sites within the interaction volume, from the energy difference of the absorption and emission maximum using fig. 2. Similarly, one can also determine n using the emission linewidth and fig. 3. Knowing n , one can infer the microscopic energy transfer parameters in equations 1 and 2 from equations 3 and 4 assuming a particular coupling mechanism and dimensionality.

Absorption and emission spectra of BCN

The absorption and emission spectra of the $T_1 - S_0$ transition of BCN at 4.2 K are shown in fig. 4. The spectra were recorded in a similar manner to, and are in agreement with, those reported in ref. 5. The absorption spectrum was fit with a Gaussian profile centered at 20284 cm^{-1} and with $\Gamma = 32 \text{ cm}^{-1}$. The calculated trapped emission spectrum shown in fig. 4 is that for $n = 365$ sites and is found

to be in good agreement with the observed spectrum. We now discuss this interaction volume in terms of the different energy transfer mechanisms which might be expected to be important for BCN.

The naphthalene skeleton of the different BCN molecules are stacked along a one dimensional array⁷, similar to the 1,4-dibromonaphthalene (DBN) crystal for which the triplet exciton dynamics are found to be one dimensional and to occur through exchange coupling with a nearest neighbor interaction, β , of 7.4 cm^{-1} .⁸ The 365 sites contained in the interaction volume would yield an interaction radius, R_0 , of 182 for a one dimensional interaction. Using $\beta = 7.4 \text{ cm}^{-1}$, $R_0 = 182$, and $\tau_0 = 20 \text{ msec}$ ⁹ for BCN one obtains from equ. 3(b) a value for γd for direct 1-D exchange of 0.1. Exchange interactions are usually of shorter range, i.e. $\gamma d \gg 1$, with $\gamma d \approx 5$ being typical for many aromatic systems.¹⁰ At these relatively large donor-acceptor distances, superexchange, rather than the exchange, mechanism is expected to be dominant for the BCN system. For the superexchange mechanism the rate of energy transfer at a distance $(N+1)d$ is given by¹¹

$$W(R) = \frac{1}{\tau} \exp (N \ln (\beta / \Delta E)) \quad (7)$$

where ΔE is the separation between host and guest singlet-triplet transition energies. For BCN one can assume that ΔE in this disordered system is given by the energy separation between the absorption and emission maxima. Using $\Delta E = 76 \text{ cm}^{-1}$ and $N = 181$ one finds $\beta \approx 66 \text{ cm}^{-1}$. This value of β is about an order of magnitude larger than the value determined for DBN.⁸ This could be due to: a) the assumption used for ΔE , b) one dimensional superexchange mechanism is not dominant, c) equation (7) is not the correct one to use for a system in which ΔE is also a disorder parameter. This makes the transfer time between a particular donor-acceptor pair dependent not only on the donor-acceptor separation but also on the random energy barriers due to intervening molecules

of higher triplet energy levels. A detailed theoretical development of this important problem is needed.

We now consider possible three dimensional interactions. At low acceptor concentrations, which is the case for the region of observed emission in BCN (see fig. 4), energy transfer by weaker but more isotropic interactions may become important.¹² From $n = 365$ one obtains $R_0 = 4.5$ for a three dimensional interaction. For direct exchange in three dimensions, using $\beta \leq 7.4$ ⁻¹ as an upper limit for the isotropic exchange interaction, one obtains $\gamma d \leq 7$ using equ. 3(b). For superexchange in three dimensions using an effective $V = 76$ cm^{-1} and equ. 7 one obtains an isotropic $\beta = 0.6$ cm^{-1} . We also consider the isotropic dipole-dipole mechanism here. Using $R_0 = 4.5$ and equ. 3(a) one obtains a value for the nearest neighbor dipolar transfer time $\tau = 2.6$ μsec .

We have analyzed the emission spectrum of BCN in terms of one dimensional exchange-type interactions, as observed for the triplet exciton in the analogous DBN system, and possible three-dimensional interactions. The results suggest that the energy transfer at low concentrations in this system is three dimensional or that the approximate analysis of one-dimensional energy transfer in this system is inadequate. We could not, however, distinguish between three-dimensional exchange-type and dipole-dipole interactions. In this respect, we note that recent time resolved phosphorescence line narrowing studies of the $T_1 - S_0$ transition of BCN in the low energy region where the BCN phosphorescence is observed indicate that the energy transfer is of a three-dimensional dipole-dipole nature.⁹ From the data in ref. 9, a value of τ for dipolar coupling on the order of 1 μsec is obtained, in good agreement with the value of 2.6 μsec obtained here from the absorption and emission spectra.

Conclusions

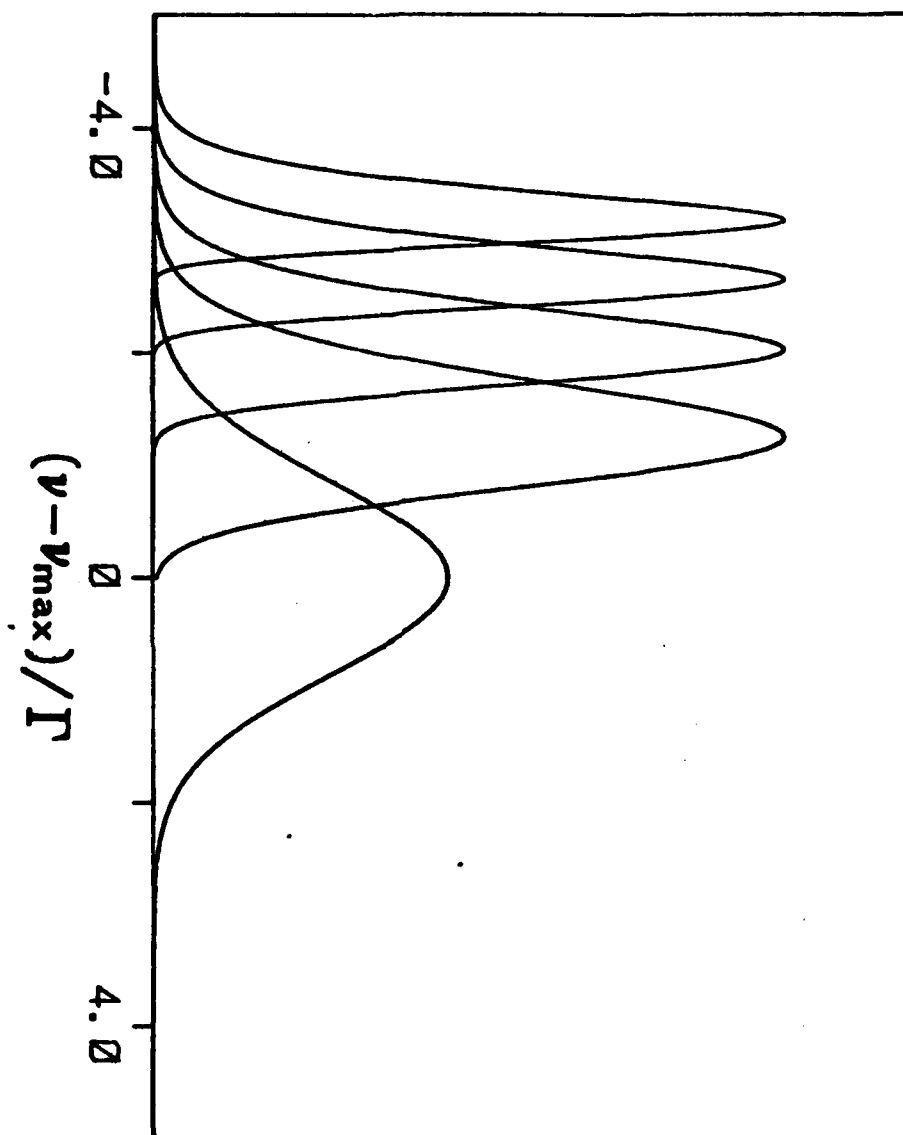
In this letter we have presented a simple, but quite general, model explaining the observed emission profile from energy trapping sites in inhomogeneously broadened systems,

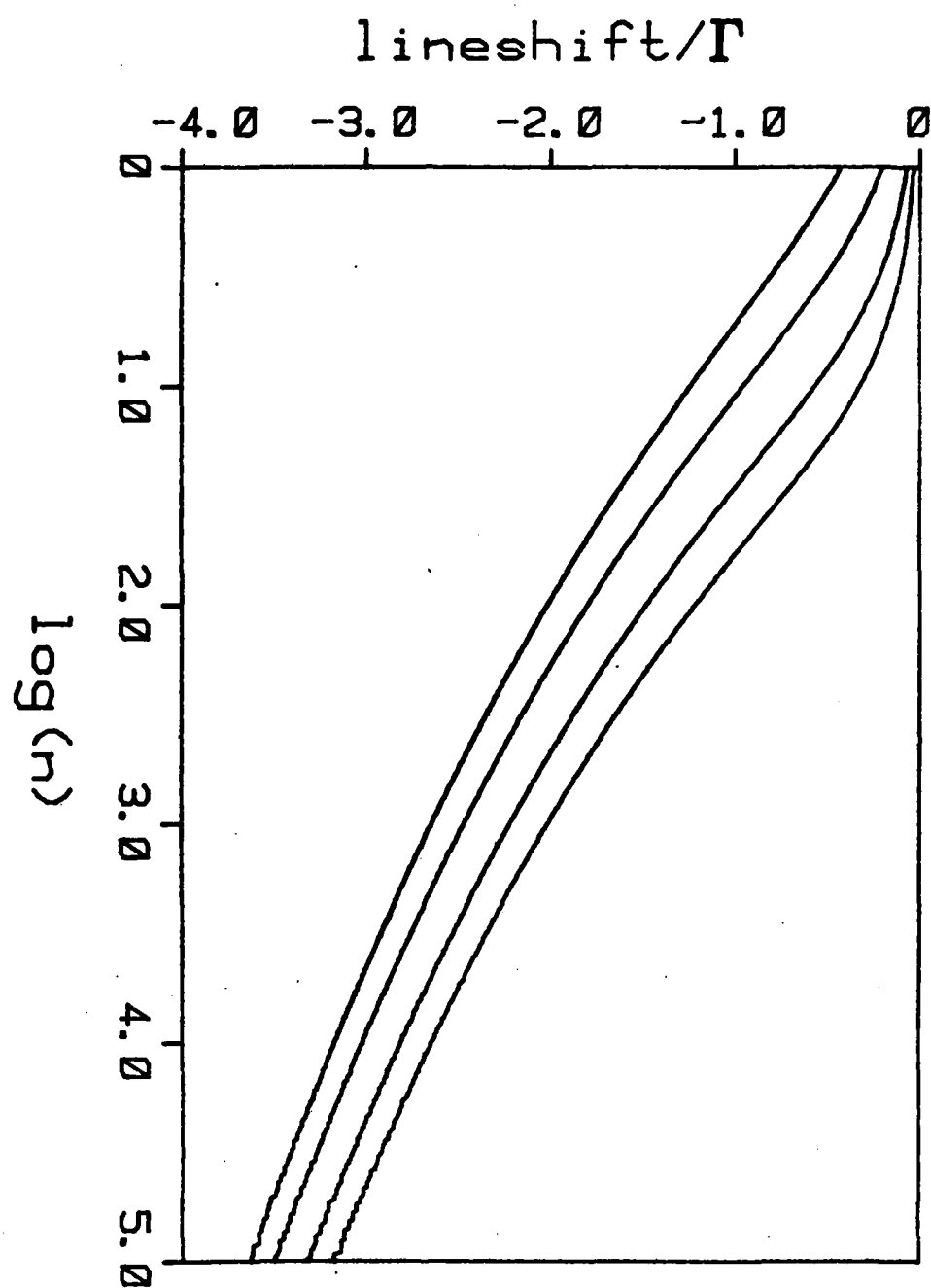
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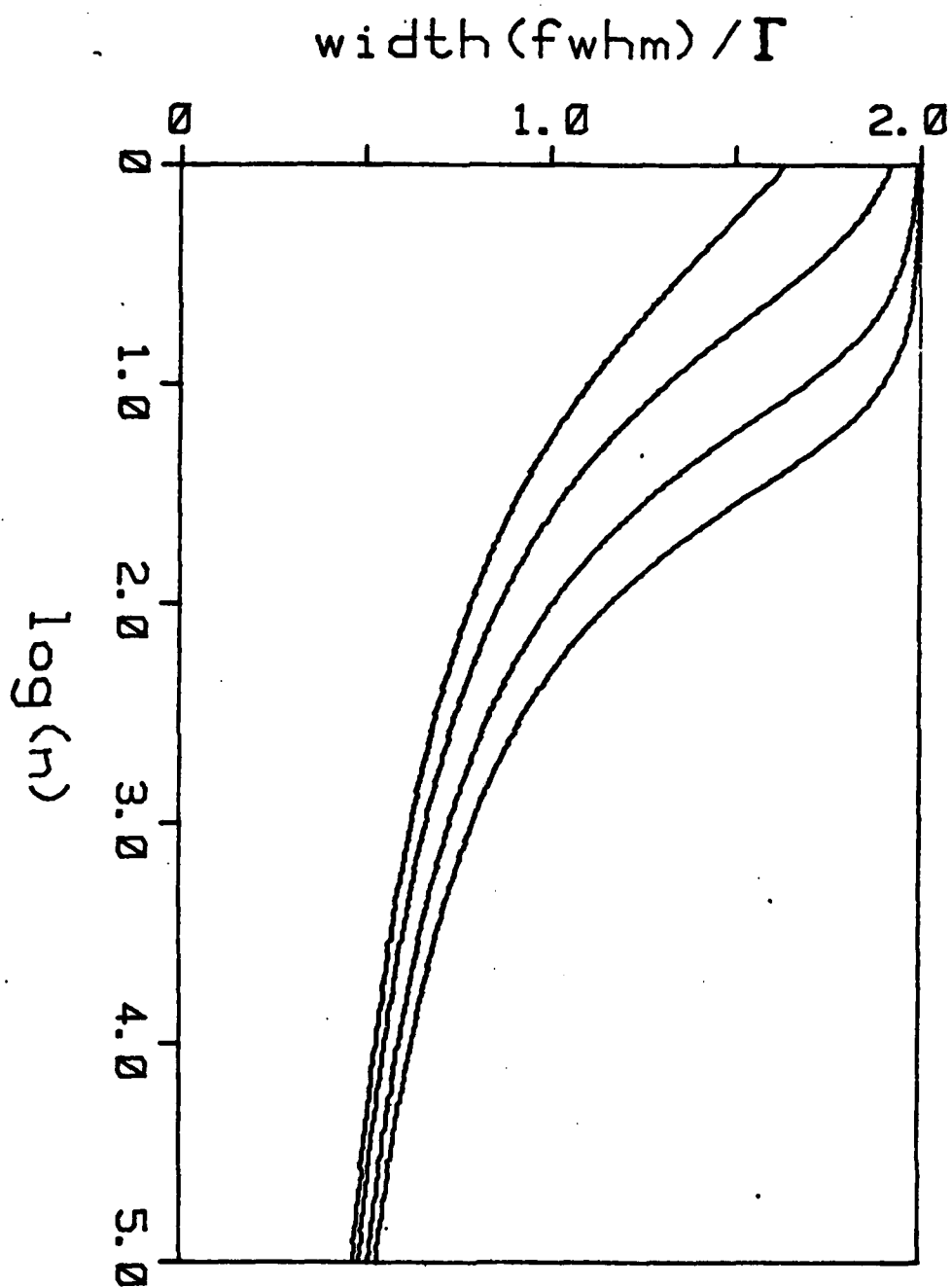
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- Fig. 1. The emission profile $I(\nu)$ for a Gaussian absorption profile in a single component crystal with an energy transfer interaction volume of n sites. Plotted from right to left are the Gaussian absorption profile and the emission profiles for $n = 10^1, 10^2, 10^3$, and 10^4 sites respectively. The emission profile is found to shift to lower energy and to narrow in width with increasing n .
- Fig. 2. The shift in the guest emission maximum from the absorption maximum normalized by the Gaussian absorption width Γ (hwhm) vs. the interaction volume n . From bottom to top, these curves are for guest mole fractions $p = 1.0, 0.5, 0.2$ and 0.1 respectively.
- Fig. 3. The guest emission linewidth (fwhm) normalized by Γ vs. the interaction volume n . From bottom to top, these curves are for guest mole fractions $p = 1.0, 0.5, 0.2$ and 0.1 respectively.
- Fig. 4. The emission and absorption spectra of the $T_1 - S_0$ transition of 1-bromo,4-chloronaphthalene (BCN) at 4.2 K. The observed absorption profile of the zero phonon line of the 0,0 band is fitted to a Gaussian centered at 20284 cm^{-1} with $\Gamma = 32 \text{ cm}^{-1}$ (solid line). The observed narrowed emission profile centered at 20208 cm^{-1} along with the calculated emission lineshape (solid line) using eq. 5 with $n = 365$ sites.

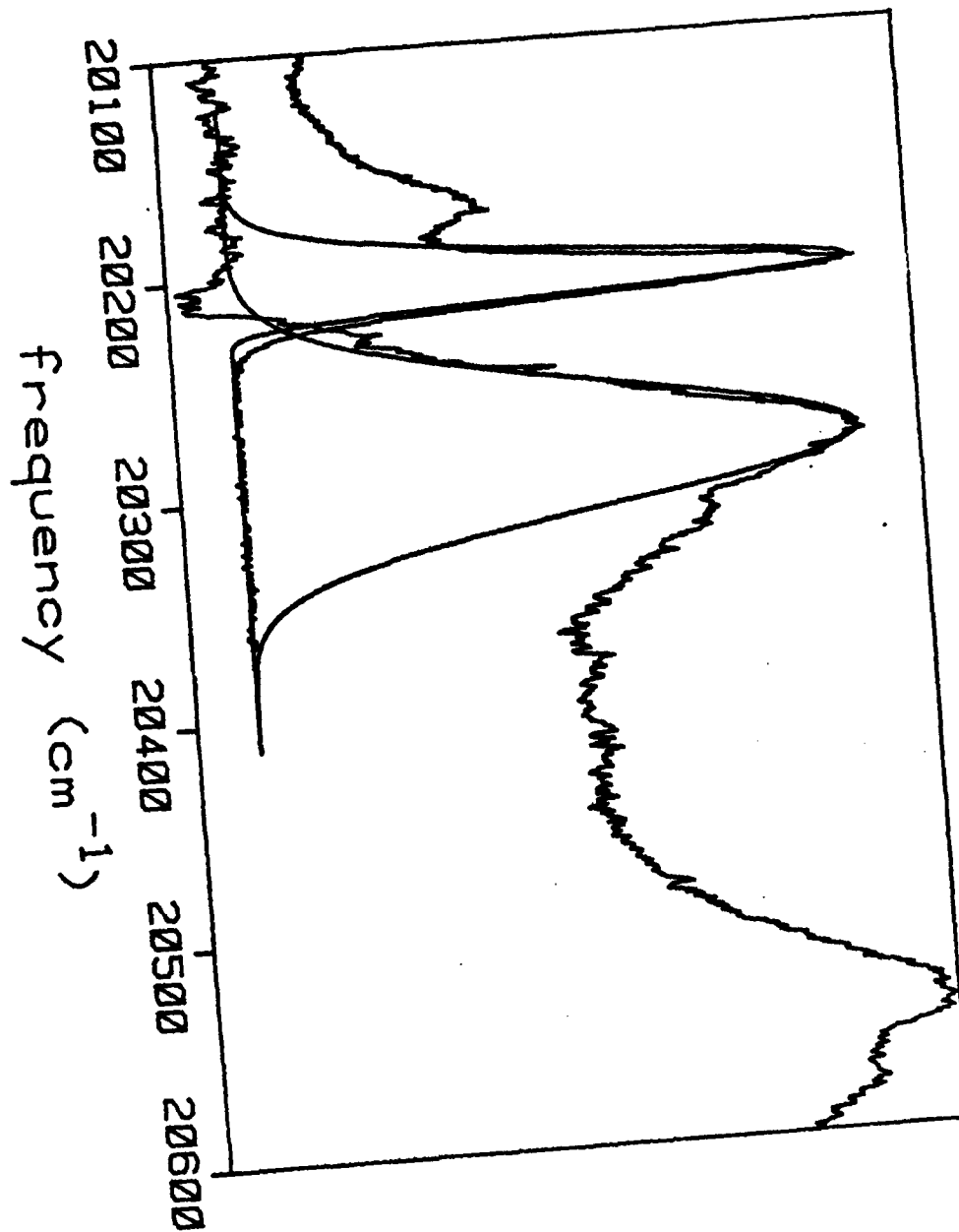
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